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In cooperation with the Kentucky Department of Agriculture

# PESTICIDES AND NUTRIENTS IN KARST SPRINGS IN THE GREEN RIVER BASIN, KENTUCKY, MAY–SEPTEMBER 2001

## MAJOR FINDINGS

- Nine different pesticides were detected in eight karst springs sampled in the Green River drainage basin.
- The five most frequently detected pesticides at all springs were atrazine (100 percent), simazine (93 percent), metolachlor (80 percent), tebuthiuron (66 percent), and prometon (58 percent).
- The pesticides detected were not necessarily the pesticides most heavily applied in the Green River drainage basin.
- Nitrite plus nitrate-nitrogen concentrations did not exceed the U.S. Environmental Protection Agency (USEPA) drinking water standard (10 milligrams per liter) at any of the eight springs.

## INTRODUCTION

Springs located in the Green River Basin, Kentucky, are valuable natural resources and important sources of public and domestic water supplies. Ground water and springs in the Green River Basin potentially are vulnerable to increased concentrations of pesticides and nitrates associated with agricultural activities, such as pesticides and nitrates, because of the presence of karst topography. The karst topography can allow rapid recharge of flow through fractures in rock and solutional conduits, providing little opportunity for natural filtering to occur. Understanding the extent and potential severity of ground-water contamination in karst areas is therefore crucial to protecting the public and water resources in the Green River Basin.

There is potential for ground-water contamination associated with the use of pesticides and fertilizers in the Green River Basin because of the extensive agricultural development of land. By sampling the water quality of karst springs and examining the use and detections of pesticides, information can be provided to better evaluate ground-water quality and agricultural nonpoint-source pollution in the Green River Basin, and assist resource managers in the planning and implementation of nonpoint-source pollution-control programs.

In 2001, the U.S. Geological Survey (USGS) began a 5-month study in cooperation with the Kentucky Department of Agriculture to evaluate the occurrence and distribution of pesticides and nutrients in springs in the Green River Basin. This paper summarizes data on the concentrations and frequency of detection of pesticides and nutrients in samples from eight selected springs and presents pesticide sales data (pounds of active ingredient) from the year 2000 as a surrogate for application rates.

Lost River Blue Hole Spring near Bowling Green, Kentucky.

## FIELD AND LABORATORY METHODS

The USGS collected pesticide and nutrient samples from eight springs (fig.1 and table 1). Samples were collected every 2 weeks during May–September 2001. General procedures for the collection of water-quality samples and equipment cleaning are described in Shelton (1994). Water samples were analyzed by the USGS National Water-Quality Laboratory in Denver, Colorado, for 50 pesticide compounds using methods described by Zaugg and others (1995). The laboratory reporting level (LRL) for detected pesticides are listed in table 2. A detailed discussion of LRL's can be found in Childress and others (1999). Nutrient samples (ammonia-nitrogen ($NH_3$-N), nitrite plus nitrate-nitrogen ($NO_2$ + $NO_3$-N), total phosphorus (TP), and orthophosphate (orthoP)) also were analyzed by the USGS National Water-Quality Laboratory using methods described in Fishman and Friedman (1989).

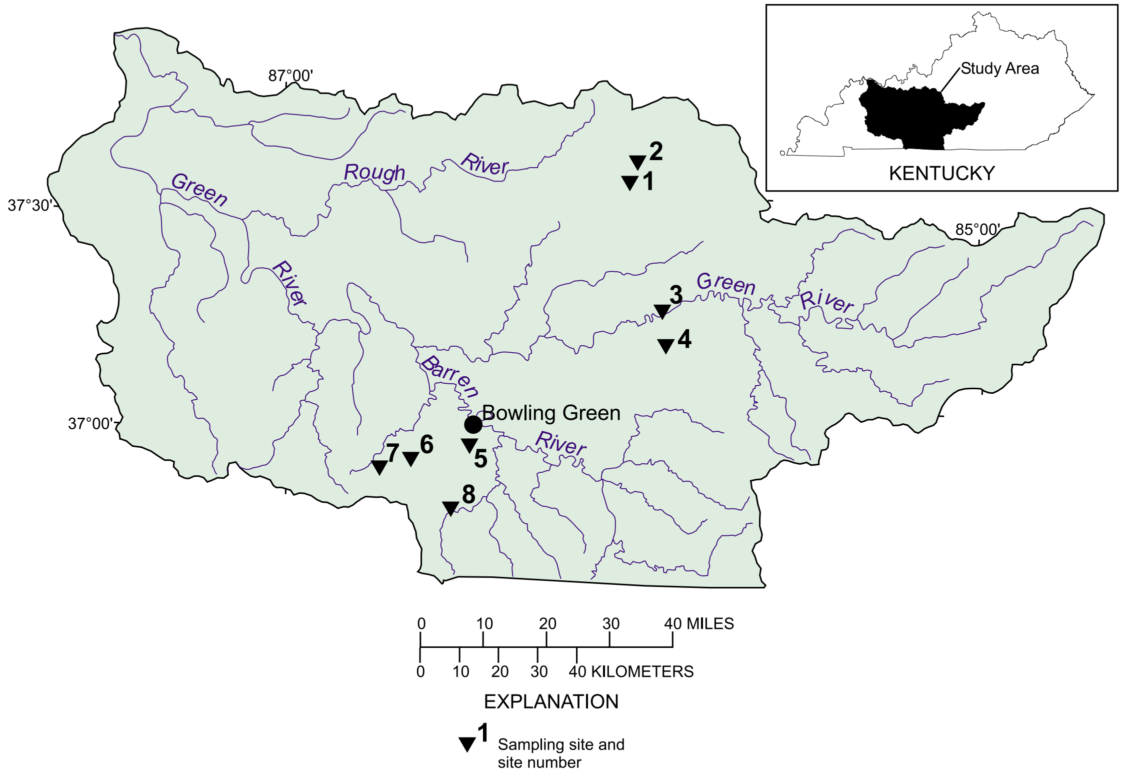


Figure **1.** Location of spring-sampling sites in the Green River Basin, Kentucky.

**Table 1.** Selected spring sampling sites in the Green River Basin, Kentucky

[USGS, U.S. Geological Survey]

| Map reference number (see fig. 1) | USGS station number | USGS station name | Latitude | Longitude | Number of samples |
|---|---|---|---|---|---|
| 1 | 373320086001601 | Waddel Spring near Harcourt, Kentucky | 37˚33’20”N | 86˚00’16”W | 8 |
| 2 | 373608085585101 | Boiling Spring at Star Mills, Kentucky | 37˚36’08”N | 85˚58’51”W | 8 |
| 3 | 371528085545301 | Gorin Mill Spring near Munfordville, Kentucky | 37˚15’28”N | 85˚54’53”W | 8 |
| 4 | 371044085542001 | Hidden River Cave at Horse Cave, Kentucky | 37˚10’44”N | 85˚54’20”W | 8 |
| 5 | 365713086282103 | Lost River Blue Hole Spring near Bowling Green, Kentucky | 36˚57’13”N | 86˚28’21”W | 8 |
| 6 | 365526086382801 | Finney Spring near South Union, Kentucky | 36˚55’26”N | 86˚38’28”W | 8 |
| 7 | 365415086435001 | Crawford Blue Hole Spring near Auburn, Kentucky | 36˚54’15”N | 86˚43’50”W | 7 |
| 8 | 364832086313701 | Drakes Spring near Woodburn, Kentucky | 36˚48’32”N | 86˚31’37”W | 8 |

**Table 2.** Summary of the concentrations, detection frequencies, and aquatic-life criteria of the detected pesticides in samples collected from eight springs, Green River Basin, Kentucky, May–September 2001

[µg/L, micrograms per liter; --, not established]

| Pesticide name | Trade name | Type of pesticide | Laboratory method reporting level (µg/L) | Detection frequency, in percent (number of samples) | Median concentration of detections (µg/L) | Maximum concentration of detections (µg/L) | Water-quality criteria for aquatic life (µg/L) |
|---|---|---|---|---|---|---|---|
| Acetochlor[d] | Harness Plus, Surpass | Herbicide | 0.004 | 14 (59) | 0.004 | 0.099 | -- |
| Atrazine[d] | AAtrex, Atred | Herbicide | .007 | 100 (59) | .159 | 7.40 | [a]1.8 |
| Chlorpyrifos | Brodan, Dursban | Insecticide | .005 | 2 (59) | .005 | .011 | [b].041 |
| Metolachlor | Dual, Pennant | Herbicide | .013 | 80 (59) | .035 | .343 | [a]7.8 |
| Metribuzin | Lexone, Sencor | Herbicide | .006 | 5 (59) | .006 | .011 | [a]1 |
| Napropamide | Devrinol, Naproguard | Herbicide | .007 | 3 (59) | .007 | .011 | -- |
| Prometon | Pramitol | Herbicide | .015 | 58 (59) | [c].014 | .468 | -- |
| Simazine | Aquazine, Princep | Herbicide | .011 | 93 (59) | .019 | .210 | [a]10 |
| Tebuthiuron | Spike, Tebusan | Herbicide | .016 | 66 (59) | [c].014 | .043 | [a]1.6 |

[a]Environment Canada, 1999
[b]U.S. Environmental Protection Agency, 1999
[c]Estimated value
[d]Restricted-use pesticide

Approximately 30 percent of the samples analyzed were quality-control samples, which included 12 field blanks, 7 concurrent replicates, 4 field spikes, and 1 laboratory blank. Field blanks were collected to ensure that no contamination occurred during sampling and processing of the samples. A blank is a type of water solution that is intended to be free of the analytes of interest. Concurrent replicates were used to evaluate the reproducibility of the laboratory analytical techniques. A concurrent replicate is a type of sample collected simultaneously by use of two or more samplers. Field-spike samples were used to determine bias as a result of matrix interference. A spike is a type of sample in which known amounts of pesticides are added to water. Quality-control-sample results indicated good laboratory performance and no systematic contamination.

## PESTICIDES

Pesticides have become an integral part of controlling insects, weeds, fungi, and bacteria in both agricultural and urban settings. The use of pesticides has increased over the last 40 to 50 years, which has resulted in increased crop production and controlled public health hazards (Larson and others, 1997); however, there are increased concerns about the possible harmful effects of increased pesticide concentrations on the environment and human health.

Of the 50 pesticides analyzed, 8 herbicides and 1 insecticide were detected at or above a common method reporting level (CMRL) of 0.01 micrograms per liter (µg/L) at the 8 springs. A CMRL allows the detection frequencies of pesticides to be compared to each other. Adjusted data, using a CMRL, were used to compare detection frequencies, whereas unadjusted data were used in statistical analyses. The detected pesticides in the springs were atrazine, simazine, metolachlor, tebuthiuron, and prometon (fig. 2). Based on estimated pesticide sales data for agricultural applications in 2000, a total of 1.5 million pounds of herbicides (fig. 3) and 18,000 pounds of insecticides (fig. 3) were applied in the Green River Basin (Ernest Collins, Kentucky Department of Agriculture, written commun., 2001).

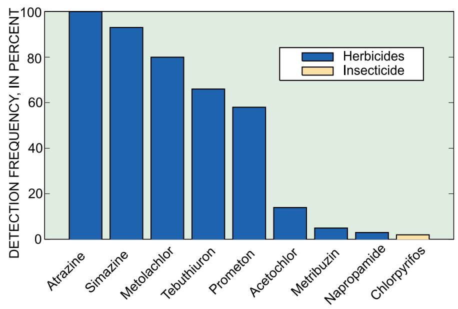


Figure **2.** Detection frequencies for selected herbicides and insecticides at eight spring-sampling sites in the Green River Basin, Kentucky.

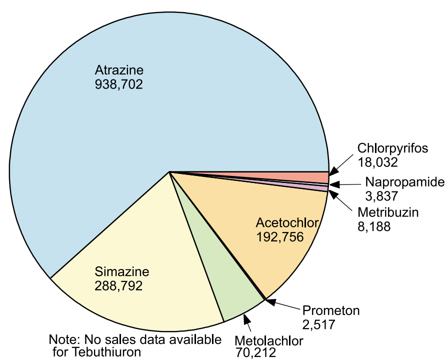


Figure **3.** Estimated sales data for 2000 (in pounds per active ingredient) of selected herbicides and insecticide in the Green River Basin, Kentucky.

The pesticides detected were not necessarily the pesticides most heavily applied (in pounds of active ingredient) in the Green River Basin. Acetochlor, a restricted-use pesticide, was found in only 14 percent of the samples, but was one of the most heavily applied pesticides (table 2 and fig. 3). It should be noted that pesticide-sales data were used as a surrogate for actual pesticide-application rates. Whereas sales data are a good indication of intended use, they do not necessarily reflect actual pesticide use (Barbash and Resek, 1996).

Only six of the listed pesticides in table 2 have an aquatic-life criterion assigned to them by the USEPA (1999a) or the Canadian Council of Resource and Environment Ministers (Environment Canada, 1999). An aquatic-life criterion is a numerical criterion designed to prevent unacceptable long-term (years and decades) and short-term (days and weeks) effects on aquatic organisms. Atrazine, a restricted-use pesticide, was the only pesticide detected at concentrations greater than its established aquatic-life criterion of 1.8 µg/L (table 2).

The maximum concentrations of four pesticides were detected in samples collected at Finney Spring: atrazine (7.40 µg/L); metolachlor (0.343 µg/l); napropamide (0.011 µg/L); and simazine (0.210 µg/L) (table 2). Maximum concentrations of acetochlor (0.099 µg/L), chlorpyrifos (0.011 µg/L), metribuzin (0.011 µg/L), and tebuthiuron (0.043 µg/L) were observed at Lost River Blue Hole Spring. The maximum concentration of prometon was observed at Gorin Mill Spring (0.468 µg/L). Median concentrations of selected pesticides ranged from 0.004 to 0.159 µg/L (table 2).

## NUTRIENTS

More than 60 water samples were collected at the eight springs and analyzed for nutrient species: ammonia-nitrogen ($NH_3$-N), nitrite plus nitrate-nitrogen ($NO_2$+$NO_3$-N), total phosphorus (TP), and orthophosphate (orthoP). Concentrations of $NH_3$-N were at or below the method reporting level of 0.04 milligrams per liter (mg/L) of N (fig. 4a), except for Crawford Blue Hole and Finney Spring.

Nitrite and nitrate are inorganic ions produced during various stages of the nitrogen cycle. Nitrate is the most predominate ion in well-oxygenated water because of the rapid oxidation of nitrite. Concentrations of nitrate

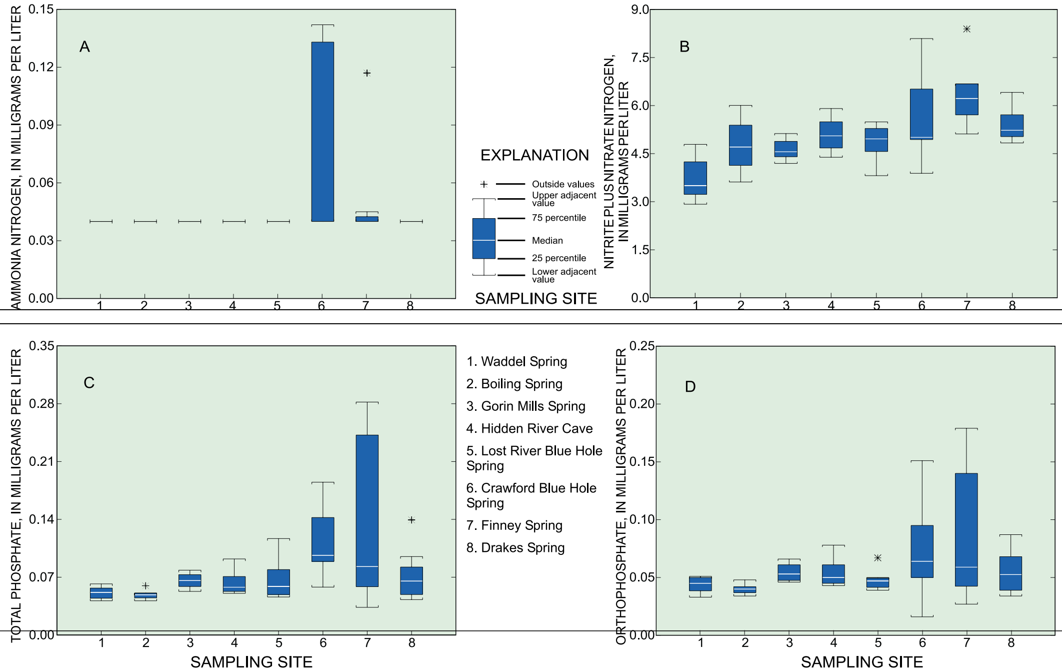


Figure **4.** Distributions of ammonia-nitrogen (A), nitrate plus nitrate-nitrogen (B), total phosphorus (C), and orthophosphate (D) concentrations in eight springs in the Green River Basin, Kentucky.

greater than 10 mg/L in drinking water can have adverse human-health effects, especially to infants whose digestive systems convert nitrate to nitrite thereby reducing the oxygen-carrying capacity of blood and resulting in methemoglobinemia (blue-baby syndrome) (U.S. Environmental Protection Agency, 1999b). Nitrite plus nitrate-nitrogen concentrations from the eight springs ranged from 2.92 to 8.39 mg/L (fig. 4b). The highest $NO_2$+$NO_3$-N concentration was measured at Finney Spring (fig. 4b). This high concentration could be a localized effect possibly caused by land use; further study is needed to determine this effect.

Although there is no established aquatic-life criterion for dissolved phosphorus, the USEPA recommends a maximum concentration of total phosphorus of 0.1 mg/L to discourage excessive growth of aquatic plants and algae. Total phosphorus concentrations in 13 percent of the samples were greater than 0.1 mg/L. The highest TP concentration among the springs sampled was 0.28 mg/L in Finney Spring (fig. 4c). The high TP concentrations possibly were associated with high values of turbidity measured at this site because phosphorus can adsorb to sediment particles. The median concentration of TP for all springs sampled was 0.06 mg/L. Orthophosphate concentrations ranged from 0.02 to 0.18 mg/L (fig. 4d).

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